STUDY ON THE PROPERTIES OF GOLD NANOPARTICLES AS PLASMONIC SENSING MATERIAL FOR CHLOROTHALONIL DETECTION

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I wish to dedicate this thesis to my late father, Razali bin Mohamed. Although he is not here to give me strength and support, I always feel his presence that used to urge me to strive to achieve my goals in life. And My mother who always had confidence in me and offered me encouragement and support in all my endeavors. To my beloved family and friends, thank you for your encouragement and support. To my supervisor and co-supervisor, thank you for your support and guidance.

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ABSTRACT

Chlorothalonil-based fungicide has been employed extensively to prevent various fungal diseases in plants to increase yield of crops. Conversely, over-usage of chlorothalonil can have adverse effects to human health and environment. An optical sensor implemented Localized Surface Plasmon Resonance (LSPR) phenomenon offers direct and simple detection method has been developed for chlorothalonil detection. In this study, a simple technique of seed-mediated growth method (SMGM) has been successfully performed to grow gold nanoparticles (GNPs) onto solid substrates. The process parameters; seeding time, growth time and effect of capping agent's molecular weight were investigated to monitor the effect on nanoparticles formation. It was found that increasing the seeding time affect the surface density of GNPs. Furthermore, the investigation on growth time shows significant impact to the shape and size of nanoparticles with 2 hours growth time formed small particles whiles 5 hours and more produces bigger particles. Moreover, in this work, molecular weight (MW) of polyvinylpyrrolidone (PVP) as shape controlling agent was also investigated to observe the uniformity of nanoparticles. PVP 55,000 produced more uniform shape and size of gold nanoparticles compared to PVP 40,000. The prepared sample with 3 hours seeding time, 8 hours growth time and 55k MW of PVP produced highest surface density of GNPs which is 53.66 ± 1.23 %. This sample was further used as a sensing material in detection of chlorothalonil. The sensitivity of the sensor system is determined by measuring the change of peak position and intensity on t-SPR and l-SPR band of GNPs in three mediums; air, deionized water and chlorothalonil solution. Chlorothalonil with 30 mM concentration (without GNPs) exhibits no significant peak and thus proven that GNPs is more suitable to be used as sensing material. Besides, GNPs shows good stability response in 600 seconds with fast response and recovery time during five cycles change of medium. As a conclusion, the GNPs was successfully synthesised and used as sensing material for chlorothalonil detection from 1mM to 40 mM.

ABSTRAK

Fungisida berasaskan klorotalonil digunakan secara meluas untuk mencegah pelbagai penyakit kulat pada tumbuh-tumbuhan untuk meningkatkan hasil tanaman. Akan tetapi, penggunaan terlalu banyak klorotalonil boleh memberi kesan buruk kepada kesihatan manusia dan alam sekitar. Sensor optik yang mengaplikasi fenomena resonans plasmon permukaan tempatan (LSPR) menawarkan kaedah pengesanan langsung dan mudah telah dibangunkan untuk pengesanan klorotalonil. Dalam kajian ini, satu kaedah mudah iaitu pertumbuhan berantara pembenihan (SMGM) telah berjaya dilakukan untuk menumbuhkan nanozarah emas (GNPs) ke atas substrat pejal. Parameter proses; masa pembenihan, masa pertumbuhan dan kesan berat molekul agen penukup telah dikaji untuk melihat kesan ke atas pembentukan nanopartikel. Didapati bahawa peningkatan masa pembenihan mempengaruhi ketumpatan permukaan GNP. Kajian ke atas masa pertumbuhan pula menunjukkan kesan yang signifikan terhadap bentuk dan saiz nanopartikel yang terhasil dengan masa pertumbuhan 2 jam membentuk zarah bersaiz kecil sementara bagi masa 5 jam dan lebih menghasilkan saiz zarah yang lebih besar. Selain itu, dalam kajian ini, berat molekul (MW) PVP sebagai agen kawalan bentuk juga dikaji untuk melihat keseragaman nanopartikel. PVP 55,000 menghasilkan bentuk dan saiz nanopartikel emas yang lebih seragam berbanding PVP 40,000. Sampel yang disediakan dengan masa pembenihan 3 jam, masa pertumbuhan 8 jam dan MW PVP 55k menghasilkan kepadatan GNP tertinggi iaitu 53.66 ± 1.23%. Sampel ini kemudiannya digunakan sebagai bahan penderia dalam pengesanan fungisida toksik iaitu klorotalonil. Kepekaan sistem sensor ditentukan dengan mengukur perubahan kedudukan puncak dan keamatan pada t-SPR dan l-SPR GNP dalam tiga medium berbeza; udara, larutan air nyahion dan larutan klorotalonil. Klorotalonil dengan kepekatan 30 mM (tanpa GNPs) menunjukkan tiada puncak yang signifikan dan dengan itu membuktikan bahawa GNPs lebih sesuai untuk digunakan sebagai bahan penderia. Selain itu, GNP sebagai bahan penderiaan menunjukkan tindak balas kestabilan yang baik dalam 600 saat dan tindak balas pengesanan serta masa pemulihan pantas dalam lima kitaran. Sebagai kesimpulan,

GNP telah berjaya disintesis dan telah digunakan sebagai bahan penderia untuk pengesanan racun kulat beracun iaitu klorotalonil pada 1 mM kepada 40 mM.

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LIST OF SYMBOLS AND ABBREVIATIONS

λ	-	Wavelength
Δ	-	Exponent
η	-	Index bias
$\pm$	-	Plus - minus
a	-	The radius of the nanospherical
ε_m	-	Dielectric constant of the surrounding medium
ε_r	-	Real part of the dielectric function of NPs
ε_i	-	Imaginary part of the dielectric function of NPs
EC_{50}	-	Median effective concentration
g/Mol	-	Molecular weight
I_d	-	The characteristic electromagnetic field decay length also known as an exponential decay
L	-	Liter
LC_{50}	-	Lethal Concentration
LD_{50}	-	Lethal Dose
m	-	Refractive index sensitivity of nanoparticles
mg	-	Milligram
Mol	-	Molarity
M	-	Molar
NOEC	-	No observed effect concentration
nm	-	Nanometer
mM	-	Millimolar
n_{medium}	-	Refractive index of the medium

n_{12}	-	Refractive index for a mixture of the two solution
N_A	-	The area density of the nanoparticles
rpm	-	Revolutions per minute
P_j	-	Depolarization factor
ppb	-	Parts per billion
μL	-	Microliter
V	-	Volume of particle
χ	-	Dynamic shape factor of the non-spherical particles
AA	-	Ascorbic acid
Ag	-	Silver
Au	-	Gold
CTAB	-	Cetyltrimethylammonium bromide
CTAC	-	Cetyltrimethylammonium chloride
DI Water	-	Deionized water
DMF	-	Dimethylformamide
EG	-	Ethylene glycol
EIA	-	Enzyme immunoassay
ELISA	-	Enzyme-linked immunosorbent assay
FESEM	-	Field emission scanning electron microscopy
GC	-	Gas chromatography
GDP	-	Gross domestic product
GNPs	-	Gold nanoparticles
GNRs	-	Gold nanorods
GNSs	-	Gold nanospheres
$HAuCl_4$	-	Gold (III) chloride trihydrate
HPLC	-	High performance liquid chromatography
LDPI	-	Laser desorption post ionization
l-SPR	-	Longitudinal surface plasmon resonance

LC	-	Liquid chromatography
LSPR	-	Localized surface plasmon resonance
MW	-	Molecular weight
$NaBH_4$	-	Sodium borohydride
NPs	-	Nanoparticles
Pd	-	Palladium
Pt	-	Platinum
PVP	-	Polyvinylpyrrolidone
RIU	-	Refractive index unit
RT	-	Room temperature
SMGM	-	Seed mediated growth method
SPR	-	Surface plasmon resonance
TOAB	-	Tetraoctylammonium bromide
t-SPR	-	Transverse surface plasmon resonance
UV-Vis	-	Ultraviolet-Visible
XRD	-	X-ray diffraction

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CHAPTER 1

INTRODUCTION

This chapter introduces the background of the study. It focuses on the problem statement and the study's objectives, which give a scholarly background and rationale for the research. The scope of the study and the organisation of the thesis are also explained.

1.1. Background study

The agriculture sector remains as a vital sector of Malaysia's economy, contributing 12% to the national gross domestic product (GDP) and offering employment for 16% of the Malaysian population, as stated in the official portal of Department of Statistic Malaysia [1]. The three main crops that dominate the agricultural exports in Malaysia are cocoa, palm oil and rubber. In addition to these products, Malaysian farmers produce fruits and vegetables for the domestic market, including cabbage, pineapples, bananas, cucumber, coconuts, rice, durian and others. The rapid development of the agricultural sector is contributed by the tropical climate in Malaysia, which is very suitable for the production of numerous exotic fruits and vegetables, especially since Peninsular Malaysia rarely experiences droughts or hurricanes.

In order to control the quality and quantity of agricultural products, especially agricultural foods, farmers need to use pesticides during planting. In vegetable farms, pests and diseases pose the biggest problem in vegetable production, and intensive pest management is needed to control them. The use of chemical pesticides is a common practice to control pests and diseases in vegetable farms in Malaysia. Pesticides can be divided into a few categories: insecticides (to kill insects), herbicides (to kill plants), rodenticides (to kill rodents such as rats and mice), fungicides (to kill fungus) and larvicides (to kill larvae). Despite all the advantages of using pesticides, they also cause harm to the environment and human health. If not used appropriately, pesticides can be poisonous towards humans directly, as they can accumulate as residuals in food and the environment, or can bring resistivity to pests [2]. These problems may arise due to pesticide abuse or being too dependent on them, especially if consumers do not realise the problems.

Hence, the Environmental Quality Act 1974 was enacted to control the discharge of chemical and industrial wastes including pesticides into the environment to prevent negative effects on human health and the environment. In addition, the Food Act 1983 prescribes the maximum residue levels of certain pesticides in agriculture. However, due to the lack of food processing, some agricultural foods are found exceeding the allowed measurement of pesticide's residues. Thus, there must be an easy-to-use tool to detect these toxic chemicals in the agricultural sector.

There are many methods to detect pesticides, such as chromatography [3], localised surface plasmon resonance (LSPR)-based sensor [4] and lysimeter [5]. An LSPR-based sensor offers fast response, easier setup and simple preparation compared to other methods. LPSR sensor, or known as plasmonic sensor, works based on the interaction at a specific wavelength between incident light with the surface electron of a noble nanometal as the sensing material. The phenomenon of LSPR is shown in Figure 1.1. The sensing material is the heart of the fabricated plasmonic sensor, and the commonly used metal are gold, silver and platinum. These nanometals are popular and widely used because of their chemical properties, surface plasmon behaviour, their properties of corrosion resistance and binding capability to biomolecules [6]–[8].

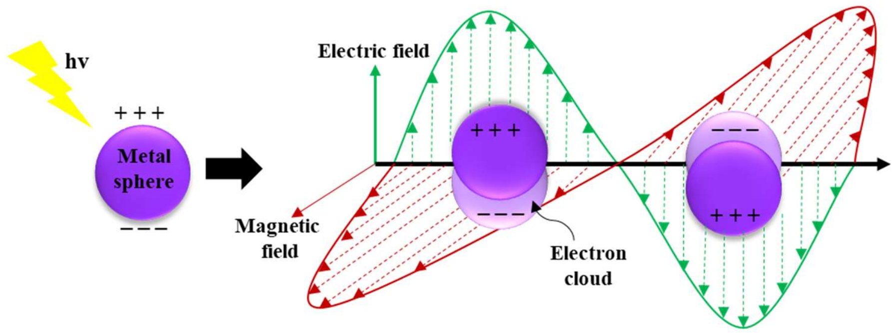

Figure 1.1: The phenomenon of LSPR of gold nanoparticles (GNPs) due to oscillation of surface electrons with incident light at specific wavelength [9]

LSPR adsorption characteristics are highly dependent on particle shape and size. For particles shape, gold nanospheres (GNSs) are the most commonly used sensing material in the plasmonic sensor due to their simple and easy preparation and synthesis method [9], [10] and that they exhibit one plasmon band associated with transverse surface plasmon resonance (t-SPR). Transverse surface plasmon resonance is a wavelength corresponding to the absorption and scattering of a wavelength of light along the short axis of the particles. Thus, the absorption strength of metal nanospheres is weak and dependent on their size, which limits their application in sensors [11]. Introducing anisotropy into the nanoparticles can make a substantial change in their magnetic properties [12], [13]. Therefore, GNPs with anisotropic structure have been chosen to solve the drawbacks of GNS's optical properties.

GNPs with anisotropic structure have exceptional optical plasmon properties with dual-band surface plasmon resonance peaks: one corresponding to the transverse plasmon mode and the other peak corresponding to the longitudinal plasmon mode [14]. As mentioned previously, t-SPR occurs at a shorter wavelength corresponding to the absorption and scattering of light along the short axis of the nanoparticles, while longitudinal surface plasmon resonance (l-SPR) is at a wavelength corresponding to the absorption and scattering of light along the long axis of the particles. This LSPR shows great potential in the applications of plasmonic sensing, drug delivery, biological imaging, photothermal therapy and catalysis.

Anisotropic GNPs such as nanorods [15], nanorices [16] and nanobipyramids [17] are commonly synthesised in solution form due to their difficulty to attach onto the substrate surface. Even though these anisotropic GNPs produce dual-band responses, maintaining their stability is crucial since they are in solution form. Therefore, there is a need to fabricate anisotropic GNPs as a thin film. The advantages of GNPs in a thin film are that it can be used multiple times and it is more stable than in solution form as the shape will not change over time. Thus far, only a few anisotropic GNPs have been fabricated as a thin film, such as nanoplates and nanotriangle. These GNP thin films have been widely used in plasmonic sensors to detect a variety of pesticides, diseases and many more.

Many conventional and nano-technological methods have been proposed for film fabrication. The process can be categorised into two approaches, which are physical [18] and chemical approaches [19]. Lithography and evaporation-condensation are examples of the physical method. Various metals have previously been produced using the evaporation-condensation method, such as gold (Au), silver (Ag), fullerene, plumbum (Pb) and platinum (Pt) [20]. However, this method requires high-cost equipment, consumes a great deal of energy while increasing the surrounding temperature of the furnace, and has extensive preparation time. On the other hand, the chemical approach is simpler but needs thoroughness to control the chemical reactions. Seed-Mediated Growth Method (SMGM) is a wet chemical synthesis approach that is able to produce nanoparticles in high yield with varying size, shape and structure [20–22]. In addition, this method can be carried out in room temperature with a simple experiment preparation and lower cost compared to the physical method.

In this study, a wet chemical synthesis technique, namely SMGM, was used to fabricate GNPs onto the substrate surface. Three parameters were studied during sample optimisation to get the most optimum thin film. The most optimum parameters were used to fabricate the thin film to be used as a sensing material in the plasmonic sensor to detect a type of fungicide, namely chlorothalonil. This fungicide is used widely in crop protection to control fungus that threatens vegetables, ornamentals, small fruits, plants and other agricultural crops.

1.2. Problem statement

Chlorothalonil is an organochlorine non-systemic fungicide used to control a wide range of fungal diseases in a variety of crops, such as cabbage, lettuce, cucumber and others. It is very toxic and long-term exposure can cause hyperplasia and tumours in the forestomach and/or kidney, as declared by the FAO/WHO Expert Committee [24]. In conjunction with the committee's report, the Malaysian government has controlled the level of chlorothalonil in food, with very low concentration under the Food Act 1983 and Table 16 of Food Regulations 1985 [25], [26]. However, due to the lack of food processing, some agricultural foods were found exceeding the allowed measurement of this pesticide's residue. Thus, there must be an easy-to-use tool to detect this toxic chemical in foods. LSPR sensor is one of the promising solutions due to its easy setup, simple preparation and most importantly its fast response compared to other conventional techniques. Other techniques used are chromatography [27], [28], electrochemical biosensor [29], fluorometric detection and lysimeter [5], [30], [31]. The drawbacks of these detection methods are that they are less sensitive, require an expensive system setup, are non-portable and have complex procedures.

For the LSPR sensor, GNPs have been widely used as a sensing material as they present fascinating optical properties due to the phenomenon of surface plasmons. Gold nanosphericals (GNSs) are commonly used in the plasmonic sensor as a sensing material due to their simple and well-developed synthesis procedures. However, the spherical particles have limitations due to their surface plasmon (SP) properties that exhibit only one SP band in the visible region, i.e., transverse plasmon band (t-SPR) [32]. Thus, there is a need to have additional sensing parameters to improve the sensitivity of the sensor. Anisotropic structures of GNPs such as nanorods [33], nanocubes [34] and nanotriangles [35] have been proposed, which provide an additional sensing parameter contributed by their longitudinal plasmon band (l-SPR). Mostly, samples of anisotropic structures are in solution form due to the structure's difficulty to attach onto the substrate surface. The synthesis process needs an additional linker material to grow the particles as a thin film and this process takes a long time to complete [36]. Thus far, only a few shapes, such as nanoplates [37], have been grown on thin films. The advantages of thin-film nanoparticles compared to the solution are their good stability and repeatability behaviour.

In this study, the GNP thin film was synthesised using a wet chemical synthesis, namely SMGM. In synthesising GNPs, there are many shapes produced, such as triangular, square, hexagon, rod, semi-hexagon and sphere. They have a broad optical

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